EVALUATOR:

- (1) Potassium butanoate (potassium butyrate); Franzosini, P., (C₄H₇O₂)₂K₂; [589-39-9] Dipartimento di
- (2) Magnesium butanoate (magnesium butyrate); Universita di Pavia (ITALY). (C4H7O2)2Mg; [556-45-6]

Franzosini, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied only by Pochtakova (Ref. 1) who, on the basis of her visual polythermal and DTA results, asserted the occurrence of a congruently melting intermediate compound, i.e., $(C_4H_7O_2)_4K_2Mg$, forming (possibly simple) eutectics with either component.

Component 1, however, goes through the liquid crystalline state before transformation into a clear melt. Therefore, the topology of the phase diagram at $0 \le 100x_2 \le 50$ should be described more correctly with reference to Scheme B.1 of the Preface, and an invariant type M'p (undetected by Pochtakova) should also exist.

The following points are still worth mentioning.

- (i) Pochtakova's fusion temperature of component 1 (677 K) coincides with the clearing temperature (677.3+0.5 K) listed in Preface, Table 1 for the same component, whereas her $T_{fus}(2)$ value (575 K) is noticeably higher than data by other authors reported in Ref. 2.
- (ii) Among the phase transformation temperatures of component 1 quoted in Ref. 1 from Ref. 3 (i.e., 618, 553-558, and 463 K) the first one can be reasonably identified with the fusion temperature $(626.1\pm0.7~\text{K})$ listed in Preface, Table 1, whereas the second and third ones lie each halfway between the two pairs of solid state transition temperatures (i.e., 562.2 ± 0.6 and 540.8 ± 1.1 , and 467.2 ± 0.5 and 461.4 ± 1.0 , respectively) also reported in Table 1 of the Preface.
- (iii) No explanation is given by the author for the discontinuities observed at temperatures (643 and 624 K, respectively) far above the liquidus in the DTA traces taken at $100x_2$ = 25 and 50.
- (iv) The author's explanation, that the discontinuities observed at temperatures corresponding to the lowest section of the subsolidus might be due to transformation (at about 445 K) of the intermediate compound into a metastable phase turning to stable at 370-400 K, should be more detailed and setter supported.

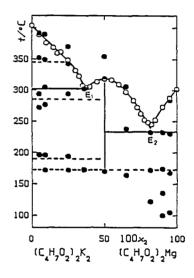
In conclusion it seems to the evaluator that the composition of the intermediate compound, the location of both eutectics, the liquidus dome, and the liquidus branch richest in component 2 are sufficiently well assessed, whereas the remaining part of the diagram needs several refinements to become satisfactory.

- (1) Pochtakova, E.I.
 Zh. Obshch. Khim. 1974, 44, 241-248.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115.
- (3) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

COMPONENTS: ORIGINAL MEASUREMENTS: (1) Potassium butanoate (potassium Pochtakova, E.I. Zh. Obshch. Khim. 1974, 44, 241-248. butyrate); (C₄H₇O₂)₂K₂; [589-39-9] (2) Magnesium butanoate (magnesium butyrate); $(C_{4}H_{7}O_{2})_{2}Mg$; [556-45-6] VARIABLES: PREPARED BY: Temperature. Baldini, P.

EXPERIMENTAL VALUES:

EXPERIMENTAL VALUES:					
t/°C	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
404	677	0	318 ^{bc}	591	50
389	662	5	170bh	443	50
392bc	665	5	354b1	627	50
20700	567	5	316	589	55
10601	469	5	309	582	60
2720]	545	5	297	570	65
່ ຊຽງDK.	625	5 5	306 ^{bc}	579	65
SOUDC	663	9	ევgbe	511	65
305DQ	578	9	164 ^{bh}	445	65
172DN	445	9	283	556	70
19601	469	9	272	545	72.5
277D.]	550	9	262	535	75
349 ^{bk}	622	9	252	525	77.5
376	649	10	248	521	80
368	641	15	232 ^{bc}	505	81.5
359	632	17.5	232be	505	81.5
361	634	20	122bf	395	81.5
348	621	25	172 ^{bh}	445	81.5
342bc	575	25	245	518	82.5
294 ^{bd}	567	25	252	525	85
172 ^{bh}	445	25	268	541	90
194 ^{bi}	467	25	273bc	546	90
370 ^{b1}	643	25	232 ^{be}	505	90
331	604	30	100 ^{bf}	373	90
322	595	32.5	136 ^{bg}	409	90
307	580	35	174 ^{bh}	447	90
302bc	575	36	288	561	95
302bd	575	36	284 ^{bc}	557	95
173 ^{bh}	446	36	230be	503	95
304	577	37.5	105bf	378	95
305	578	40	168 ^{DN}	441	95
313	586	45	302	575	100
317	590	50			



```
\overset{a}{\text{b}} T/K values calculated by the compiler. \overset{b}{\text{b}} Differential thermal analysis.
```

C Initial crystallization.

d First eutectic stop.

e Second eutectic stop.
f First transition of the system.

g Second transition of the system.

h Third transition of the system.

i Fourth transition of the system.

J Fifth transition of the system.

k Sixth transition of the system.

Seventh transition of the system (no explanation if offered by the author for the occurrence of this point above the liquidus, compiler).

COMPONENTS: ORIGINAL MEASUREMENTS: (1) Potassium butanoate (potassium Pochtakova, E.I. Zh. Obshch. Khim. 1974, 44, 241-248. butyrate); (C₄H₇O₂)₂K₂; [589-39-9] (2) Magnesium butanoate (magnesium butyrate); $(C_4H_7O_2)_2Mg$; [556-45-6] VARIABLES: PREPARED BY: Baldini, P. Temperature. EXPERIMENTAL VALUES: (continued) Characteristic point(s): Eutectic, E₁, at 300 $^{\rm o}$ C (302 $^{\rm o}$ C by D.T.A.), and $100x_2$ = 36.0 (author). Eutectic, E₂, at 235 $^{\rm o}$ C (232 $^{\rm o}$ C by D.T.A.), and $100x_2$ = 81.5 (author). Intermediate compound(s): (C7H4O2)4K2Mg, congruently melting at 318 °C. AUXILIARY INFORMATION SOURCE AND PURITY OF MATERIALS: METHOD/APPARATUS/PROCEDURE: Materials prepared (Ref. 1) by reacting the proper ("chemically pure") carbonate with a Visual polythermal analysis, supplemented with differential thermal analysis. slight excess of n-butanoic acid of analytical purity. Component 1 undergoes phase transitions at $t_{trs}(1)/^{O}C = 190$, 280-

ESTIMATED ERROR:

285, 345 (Ref. 2).

Temperature: accuracy probably ± 2 K (compiler).

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sokolov, N.M.

 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

(1) Potassium butanoate (potassium butyrate); (C4H7O2)K; [589-39-9]

(C₄H₇O₂)K; [589-39-9] (2) Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7]

EVALUATOR:

Franzosini, P., Dipartimento di Chimica Fisica Universita di Pavia (ITALY).

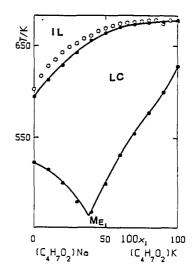
CRITICAL EVALUATION:

The visual polythermal method was employed by Sokolov and Pochtakova (Ref. 1), and by Dmitrevskaya (Ref. 2) to study the lower boundary of the isotropic liquid field: according to these authors, continuous series of solid solutions ought to exist.

Both components, however, form liquid crystals. Consequently: (1) the fusion temperatures, $T_{\rm fus}(1)$ = 677 K (404 °C) and $T_{\rm fus}(2)$ = 603 K (330 °C), reported in Refs. 1, 2 should be identified with the clearing temperatures; and (ii) a continuous series of liquid crystal (and not of solid) solutions should be expected.

More recently, Prisyazhnyi et al. (Ref. 3) - to whom Refs. 1, 2 seem to be unknown - carried out a derivatographical reinvestigation of the system, which allowed them to draw the lower boundaries of both the isotropic liquid, and the liquid crystal field. Their clearing [678 K (405 °C); 595 K (322 °C)] and fusion [628 K (355 °C); 523 K (250 °C)] temperatures substantially agree with the corresponding values from Preface, Table 1 (677.3±0.5, 600.4±0.2, and 626.1±0.7, 524.5±0.5 K, respectively).

Prisyazhnyi et al.'s, and Dmitrevskaya's results (filled and empty circles, respectively) are compared in the figure (IL: isotropic liquid; LC: liquid crystals). The complete phase diagram ought to be similar to that reported in Scheme C.1, and the only invariant ought to be classified as an $\rm M_{\rm E}$ point, at which equilibrium occurs among one liquid crystalline and two solid phases. The statements made in Refs. 1, 2 cannot be considered as correct, whereas Prisyazhnyi et al.'s measurements look as compatible with expectation.



The latter measurements can be further commented as follows: (1) the two-phase region pertinent to the liquid crystal - isotropic liquid equilibria might be so narrow as to prevent observation of two distinct sets of points in this region; (11) the lack of information about eutectic fusion in the different samples submitted to derivatographical analysis remains, however, rather surprising.

(continued in the next page)

- (1) Potassium butanoate (potassium butyrate); $(C_4H_7O_2)K$; [589-39-9]
- (2) Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7]

EVALUATOR:

Franzosini, P., Dipartimento di Chimica Fisica Universita' di Pavia (ITALY).

CRITICAL EVALUATION: (continued)

Finally, the following two points deserve attention.

(1) Among the phase transformation temperatures of component 1 quoted in Refs. 1, 2 from Ref. 4 (i.e., 618, 553-558, and 463 K) the first one can be reasonably identified with the fusion temperature (626.1 ± 0.7 K) listed in Preface, Table 1, whereas the second and third ones lie each halfway between the two pairs of solid state transition temperatures (i.e., 562.2 ± 0.6 and 540.8 ± 1.1 , and 467.2 ± 0.5 and 461.4 ± 1.0 , respectively) also reported in Table 1 of the Preface.

(ii) For component 2, Table 1 of the Preface [besides the clearing temperature] provides solid state transitions at 450.4+0.5, 489.8+0.2, 498.3+0.3, and 508.4+0.5, and fusion at 524.5+0.5. It is to be stressed that these phase relations, first stated on the basis of DSC records, were subsequently confirmed by Schiraldi and Chiodelli's conductometric results (Ref. 5). On the other hand, phase transformations are quoted in Refs. 1, 2 from Ref. 4 as occurring at 390, 505, 525, and 589 K, respectively. A comparison of the two sets of data allows one to identify conveniently the two intermediate transition temperatures from Ref. 4 with the first transition temperature and the fusion temperature from Table 1, whereas reasonable doubts can be cast about the actual existence of the highest and lowest transformations quoted in Refs. 1, 2.

- (1) Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1958, 28, 1693-1700 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1741-1747.
- (2) Dmitrevskaya, 0.1.
 Zh. Obshch. Khim. 1958, 28, 2007-2013 (*); Russ. J. Gen. Chem. (Engl. Transl.)
 1958, 28, 2046-2051.
- (3) Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A. Ukr. Khim. Zh. 1983, 49, 659-660.
- (4) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (5) Schiraldi, A.; Chiodelli, G. J. Phys. E: Sci. Instr. 1977, 10, 596-599.

- (1) Potassium butanoate (potassium butyrate); (C₄H₇O₂)K; [589-39-9]
- (2) Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1958, 28, 1693-1700 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1741-1747.

VARIABLES:

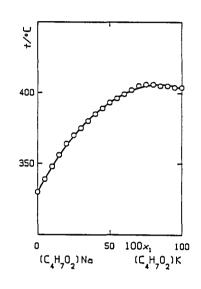
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100x ₁
330 339 348 356 364 370 375 380 385 389 393 396 399	603 612 621 629 637 643 648 653 658 662 666 669 672	0 5 10 15 20 25 30 35 40 45 50 55 60
402 405 406 406 405 405 404 404	675 678 679 679 678 678 677	65 70 75 80 85 90 95



Characteristic point(s): Continuous series of solid solutions (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Temperatures measured with a Nichrome-Constantane thermocouple.

SOURCE AND PURITY OF MATERIALS:

Components synthetized from "chemically pure" potassium and sodium hydrogen carbonates, and n-butanoic acid (Ref. 2, where, however, carbonates instead of hydrogen carbonates are employed; compiler); the salts obtained were recrystallized from n-butanol. Component 1 undergoes phase transitions at $t_{\rm trs}(1)/^{\rm C}$ = 190, 280-285, 345 (Ref. 2). Component 2 undergoes phase transitions at $t_{\rm trs}(2)/^{\rm C}$ = 117, 232, 252, 316 (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sokolov, N.M.

 Tezisy Dokl. X Nauch. Konf. S.M.I.
 1956.

a T/K values calculated by the compiler.

- (1) Potassium butanoate (potassium butyrate);
- (C₄H₇O₂)K; [589-39-9] (2) Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7]

ORIGINAL MEASUREMENTS:

Dmitrevskaya, 0.I.

Zh. Obshch. Khim. 1958, 28, 2007-2013 (*);

Russ. J. Gen. Chem. (Engl. Transl.) 1958,
28, 2046-2051.

VARIABLES:

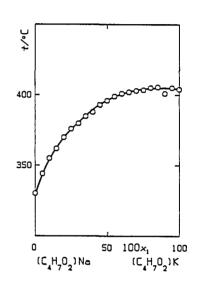
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

Dat Bittimutin		**********	
t/°C	T/K ^a	100 x 1	
330	603	0	
344	617	5	
355	628	10	
362	635	15	
370	643	20	
376	649	25	
380	653	30	
385	658	35	
388	661	40	
393	666	45	
396	669	50	
399	672	55	
401	674	60	
402	675	65	
403	676	70	
403.5	676.5	75	
405	678	80	
405.5	678.5	85	
401	674	90	
405	678	95	
404	677	100	



Characteristic point(s): Continuous series of solid solutions (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Temperatures measured with a Nichrome-Constantane thermocouple.

SOURCE AND PURITY OF MATERIALS:

Components synthetized from "chemically pure" potassium and sodium hydrogen carbonates, and n-butanoic acid twice distilled.

Component 1 undergoes phase transitions at $t_{\rm trs}(1)/^{\rm C}c=$ 190, 280-285, 345 (Ref. 1). Component 2 undergoes phase transitions at $t_{\rm trs}(2)/^{\rm C}c=$ 117, 232, 252, 316 (Ref. 1).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

REFERENCES:

(1) Sokolov, N.M.

Tezisy Dokl. X Nauch. Konf. S.M.I.

1956.

 $^{^{}m a}$ T/K values calculated by the compiler.

- Potassium butanoate (potassium butyrate);
 - $(C_4H_7O_2)K; [589-39-9]$
- (2) Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7]

ORIGINAL MEASUREMENTS:

Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A.

Ukr. Khim. Zh. 1983, 49, 659-660.

VARIABLES:

Temperature.

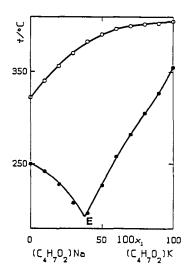
PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

The results are reported only in graphical form (see figure; data read with a digitizer by the compiler on Fig. 1 of the original paper; empty circles: liquid crystal - isotropic liquid equilibria; filled circles: solid - liquid crystal equilibria).

Characteristic point(s): Eutectic, E, at 194 °C and $100x_1$ = 38 (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The heating and cooling traces were recorded in an atmosphere of purified argon with an OD-102 derivatograph (MOM, Hungary) working at a rate of 6 K min⁻¹, and using Al₂O₃ as reference material. Temperatures were measured with a Pt/Pt-Rh thermocouple. A hot-stage Amplival polarizing microscope was employed to detect the transformation points from the liquid crystalline into the isotropic liquid phase. Supplementary information was obtained by conductometry.

SOURCE AND PURITY OF MATERIALS:

Not stated. Component 1: $t_{fus}(1)/^{o}C$ about 355; $t_{clr}(1)/^{o}C$ about 405 (compiler). Component 2: $t_{fus}(2)/^{o}C$ about 250; $t_{clr}(2)/^{o}C$ about 322 (compiler).

ESTIMATED ERROR:

Temperature: accuracy not evaluable (compiler).

- (1) Lithium butanoate (lithium butyrate);
- (C₄H₇O₂)Li; [21303-03-7] (2) Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7]

EVALUATOR:

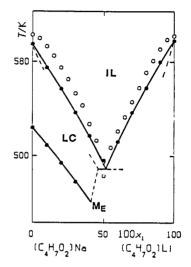
Schiraldi, A., Dipartimento di Chimica Fisica Universita di Pavia (ITALY).

CRITICAL EVALUATION:

polythermal analysis was visual employed by Tsindrik and Sokolov (Ref. 1) to study the lower boundary of the isotropic liquid field: according to these authors, a eutectic ought to exist at 495 K (222 °C), and $100x_2 = 50$.

Component 2, however, forms liquid crystals. Consequently: (1) the fusion temperature, 603 K (330 °C) reported in Ref. 1 should be identified with the clearing temperature; (ii) the two branches of the curve refer to equilibria of different kind; and (iii) the intersection of the two branches cannot be classified as a eutectic.

More recently, Prisyazhnyi et al. (Ref. 2) - to whom Ref. 1 seems to be unknown carried out a derivatographical reinvestigation of the system, which allowed them to draw the lower boundaries of both



the isotropic liquid, and the liquid crystal field. Their clearing $[T_{c1r}(2)=595~K~(322~^{\circ}C)]$ and fusion $[T_{fus}(1)=598~K~(325~^{\circ}C);~T_{fus}(2)=524~K~(251~^{\circ}C)]$ temperatures substantially agree with the corresponding values from Table 1 of the Preface $(600.4\pm0.2;~591.7\pm0.5,~and~524.5\pm0.5~K,~and~524.5~K,~and~524.5~K,~and~524.5~K,~and~524.5~K,~and~$ respectively).

Prisyazhnyi et al.'s, and Tsindrik and Sokolov's results (filled and empty circles, respectively) are compared in the figure (IL: isotropic liquid; LC: liquid crystals). Assuming that limited solid solutions are present, the complete phase diagram ought to be similar to that reported in Preface, Scheme A.1. The upper invariant ought to be classified as an M'E point, and the lower one as an ME point.

Prisyazhnyi et al.'s measurements look as compatible with expectation, although the lack of information about eutectic fusion in the different samples studied by derivatographical analysis remains rather surprising. Instead, the narrowness of the derivatographical analysis remains rather surprising. Instead, two-phase region pertinent to the liquid crystal - isotropic liquid equilibria could have prevented the observation of two distinct sets of points in this region.

Finally, the following point requires attention. For component 2, Table 1 of the Preface [besides the $T_{c1r}(2)$ value] provides four solid state transitions at 450.4±0.5, 489.8±0.2, 498.3±0.3, and 508.4±0.5 K, and $T_{fus}(2)/K=524.5±0.5$. It is to be stressed that these phase relations, first stated on the basis of DSC records, were subsequently confirmed by Schiraldi and Chiodelli's conductometric results (Ref. 3). On the other hand, phase transformations are quoted in Ref. 1 from Ref. 4 as occurring at 390, 505, 525, and 589 K, respectively. A comparison of the two sets of data allows one to identify conveniently the two intermediate transition temperatures from Ref. 4 with the first solid state transition and fusion temperatures from Table 1 of the Preface, whereas reasonable doubts can be cast about the actual existence of the highest and lowest transformations quoted in Ref. 1.

- (1) Tsindrik, N.M.; Sokolov, N.M. Zh. Obshch. Khim. 1958, 28, 1728-1733 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1775-1780.
- (2) Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A. Ukr. Khim. Zh. 1983, 49, 659-660.
- (3) Schiraldi, A.; Chiodelli, G. J. Phys. E: Sci. Instr. 1977, 10, 596-599.
- (4) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Lithium butanoate (lithium butyrate); (C₄H₇O₂)Li; [21303-03-7]
- (2) Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7]

ORIGINAL MEASUREMENTS:

Tsindrik, N.M.; Sokolov, N.M. Zh. Obshch. Khim. 1958, 28, 1728-1733 (*); Russ. J. Gen. Chem. (Engl. transl.) 1958, 28, 1775-1780.

VARIABLES:

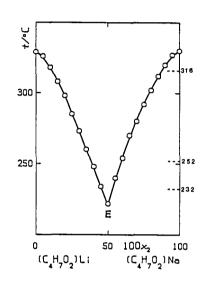
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2
329	602	0
326	599	5
318	591	10
308	581	15
298	571	20
285	558	25
273	546	30
260	533	35
248	521	40
234	507	45
222	495	50
240	513	55
254	527	60
270	543	65
280	553	70
292	565	75
302	575	80
312	585	85
320	593	90
327	600	95
330	603	100



Characteristic point(s): Eutectic, E, at 222 °C and $100x_2$ = 50 (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; temperatures of initial crystallization measured with a Nichrome-Constantane thermocouple and a millivoltmeter.

SOURCE AND PURITY OF MATERIALS:

Both components prepared from "chemically pure" carbonates and n-butanoic acid (Ref. 1); the solids recovered after evaporation were recrystallized from n-butanol. Component 2 undergoes phase transitions at $t_{\rm trs}(2)/{}^{\rm C}=117$, 232, 252, 316 (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sokolov, N.M.

 Tezisy Dokl. X Nauch. Konf. S.M.I.
 1956.

a T/K values calculated by the compiler.

- (1) Lithium butanoate (lithium butyrate); (C₄H₇O₂)Li; [21303-03-7]
- (2) Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7]

ORIGINAL MEASUREMENTS:

Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A. Ukr. Khim. Zh. 1983, 49, 659-660.

VARIABLES:

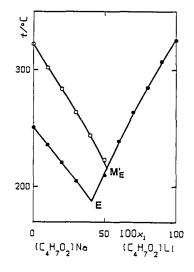
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

The results are reported only in graphical form (see figure). Data read with a digitizer by the compiler on Fig. 1 of the original paper; empty circles: liquid crystal - isotropic liquid equilibria; filled circles: solid - liquid crystal or solid - isotropic liquid equilibria).



Characteristic point(s):

Eutectic, E, at 188 $^{\rm o}$ C and $100{\rm x_1}$ = 41 (authors). Invariant point, M' $_{\rm E}$, at about 215 $^{\rm o}$ C and $100{\rm x_1}$ about 52 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The heating and cooling traces were recorded in an atmosphere of purified argon with an OD-102 derivatograph (MOM, Hungary) working at a rate of 6 K min⁻¹, and using Al₂O₃ as the reference material. Temperatures were measured with a Pt/Pt-Rh thermocouple. A hot-stage Amplival polarizing microscope was employed to detect the transformation points from the liquid crystalline into the isotropic liquid phase. Supplementary information was obtained by conductometry.

SOURCE AND PURITY OF MATERIALS:

Not stated. Component 1: $t_{fus}(1)/^{o}C$ about 325 (compiler). Component 2: $t_{fus}(2)/^{o}C$ about 251; $t_{c1r}(2)/^{o}C$ about 322 (compiler).

ESTIMATED ERROR:

Temperature: accuracy not evaluable (compiler).

- (1) Magnesium butanoate (magnesium butyrate);
- (C₄H₇O₂)₂Mg; [556-45-6] (2) Sodium butanoate (sodium butyrate); (C₄H₇O₂)₂Na₂; [156-54-7]

EVALUATOR:

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CRITICAL EVALUATION:

This binary was studied only by Pochtakova (Ref. 1) who (on the basis of visual polythermal and DTA results) claimed the occurrence of the congruently melting intermediate compound $({}^{C}_4{}^{H}_7{}^{O}_2)_7$ Mg $_2{}^{N}{}^{a}_3$, able to give eutectics with either component.

Component 2, however, goes through the liquid crystalline state before transformation into a clear melt. Therefore the topology of the phase diagram at $0 \le 100 \mathbf{x}_1 \le 57$ should be described more correctly with (probable) reference to Preface, Scheme $\overline{A} \cdot \overline{1}$: in this case the invariant ought to be of the M_E' type.

The following points are still worth mentioning.

- (i) Pochtakova's fusion temperature of component 1 (575 K) is noticeably higher than data by other authors reported in Ref. 2, whereas her $T_{fus}(2)$ value (603 K) is in reasonable agreement with the clearing temperature (600.4 \pm 0.2 K) listed in Preface, Table 1 for component 2.
- (ii) Again for component 2, Table 1 of the Preface provides four transition temperatures (450.4±0.5, 489.8±0.2, 498.3±0.3, and 508.4±0.5 K), and $T_{fus}(2)/K=524.5±0.5$. It is to be stressed that these phase relations, first stated on the basis of DSC records, were subsequently confirmed by Schiraldi and Chiodelli's conductometric results (Ref. 3). On the other hand, phase transformations are quoted in Ref. 1 from Ref. 4 as occurring at 390, 505, 525, and 589 K, respectively. A comparison of the two sets of data allows one to identity conveniently the two intermediate transition temperatures from Ref. 4 with the highest solid state transition and fusion, respectively, from Table 1 of the Preface, whereas reasonable doubts can be cast about the actual existence of the highest and lowest transformations quoted by Pochtakova.
- (iii) In the DTA traces taken at $100\mathbf{x}_1$ = 10 and 35, Pochtakova observed discontinuities at 587 and 573 K, and at 528 and 507 K, respectively, which might correspond to the higher (587 and 528 K) and lower (573 and 507 K) boundary of a diphasic region, thus supporting an interpretation of the phase diagram based on Scheme A.1 of the Preface.
- (iv) The author's explanation, that the discontinuities observed at temperatures corresponding to the lowest section of the subsolidus might be due to the transformation (at about 435 K) of the intermediate compound into a metastable phase turning to stable at about 410 K, should be more detailed and better supported.

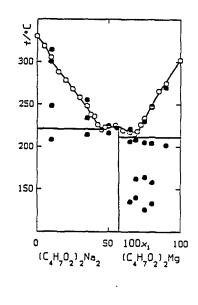
In conclusion, it seems to the evaluator that the existence of an intermediate compound, the location of both eutectics, and the liquidus branch richest in component 1 are sufficiently well assessed, whereas other parts of the diagram need refinements.

- (1) Pochtakova, E.I.
 Zh. Obshch. Khim. 1974, 44, 241-248.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115.
- (3) Schiraldi, A.; Chiodelli, G. J. Phys. E: Sci. Instr. 1977, 10, 596-599.
- (4) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

COMPONENTS: ORIGINAL MEASUREMENTS: Pochtakova, E.I. Zh. Obshch. Khim. 1974, 44, 241-248. (1) Magnesium butanoate (magnesium butyrate); (C₄H₇O₂)₂Mg; [556-45-6] (2) Sodium butanoate (sodium butyrate); $(C_4H_7O_2)_2Na_2$; [156-54-7] VARIABLES: PREPARED BY: Temperature. Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 1			
330	603	0	217	490	65
318	591	5	220bc	493	65
305	578	10	206 ^{be}	479	65
300pc	573	10	135 ^{bf}	408	65
208 ^{bd}	481	10	215	488	67.5
248 ^{b1}	521	10	208 ^{bc}	481	69
314 ^b j	587	10	208 ^{be}	481	69
288	561	15	140 ^{bf}	413	69
278	551	20	162 ^{bg}	435	69
268	541	25	218	491	70
258	531	30	226	499	72.5
248	521	35	234	507	75
255bc	528	35	230 ^{bc}	503	75
214bd	487	35	205be	478	75
234 ^{bh}	507	35	126bf	399	75
238	511	37.5	164 ^{bg}	437	75
236	509	40	247	520	80
226	499	42.5	248bc	521	80
220	493	45	204be	477	80
220bc	493	45	133bf	406	80
220 ^{bd}	493	45	158 ^{bg}	431	80
223	496	47.5	266	539	85
224	497	50	275	548	90
225bc	498	50	270bc	543	90
216 ^{bd}	489	50	202 ^{be}	475	90
225 225	498	55	138 ^{bf}	411	90
222bc	495	55	302	575	100



a T/K values calculated by the compiler.

b Differential thermal analysis (filled circles in the Figure).

All other data are from visual polythermal analysis and are represented as empty circles in the Figure.

c Initial crystallization.

d Eutectic stop (E2).

492

219

e Eutectic stop (E₁).
f First transition of the system.

g Second transition of the system.

Third transition of the system.

i Fourth transition of the system.

j _{Fifth} transition of the system (no explanation if offered by the author for the occurrence of this point above the liquidus, compiler).

(continued in the next page)

COMPONENTS: (1) Magnesium butanoate (magnesium butyrate); (C₄H₇O₂)₂Mg; [556-45-6] (2) Sodium butanoate (sodium butyrate); (C₄H₇O₂)₂Na₂; [156-54-7] VARIABLES: Temperature. CORIGINAL MEASUREMENTS: Pochtakova, E.I. Zh. Obshch. Khim. 1974, 44, 241-248. PREPARED BY: Baldini, P. EXPERIMENTAL VALUES: (continued)

Characteristic point(s):

Eutectic, E_1 , at 210 °C (208 °C by DTA), and $100x_1$ = 69 (author). Eutectic, E_2 , at 220 °C and $100x_1$ = 45 (author).

Intermediate compound(s):

 $(\text{C}_4\text{H}_7\text{O}_2)_7\text{Mg}_2\text{Na}_3$ (author), congruently melting at 225 $^{\text{O}}\text{C}$ (as reported in Ref. 1, Fig. 1, compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis, (empty circles in the Figure) supplemented with DTA (filled circles).

SOURCE AND PURITY OF MATERIALS:

Materials prepared (Ref. 2) by reacting the proper ("chemically pure") carbonate with a slight excess of butanoic acid of analytical purity. Component 2 undergoes phase transitions at $t_{trs}(2)/^{o}C=117$, 232, 252, 316 (Ref. 3).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

- (1) Pochtakova, E.I. Zh. Obshch. Khim. 1978, 48, 1212-1214.
- (2) Sokolov, N.M.

 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (3) Sokolov, N.M.; Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.